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Exciton Transfer Integrals Between Polymer Chains

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The line-dipole approximation for the evaluation of the exciton transfer integral, J, between conjugated polymer chains is rigorously justified. Using this approximation, as well as the plane-wave approximation for the exciton center-of-mass wavefunction, it is shown analytically that $J \sim L$ when the chain lengths are smaller than the separation between them, or $J \sim L^{-1}$ when the chain lengths are larger than their separation, where L is the polymer length. Scaling relations are also obtained numerically for the more realistic standing-wave approximation for the exciton center-of-mass wavefunction, where it is found that for chain lengths larger than their separation $J \sim L^{-1.8}$ or $J \sim L^{-2}$, for parallel or collinear chains, respectively. These results have important implications for the photo-physics of conjugated polymers and self-assembled molecular systems, as the Davydov splitting in aggregates and the Förster transfer rate for exciton migration decreases with chain lengths larger than their separation. This latter result has obvious deleterious consequences for the performance of polymer photovoltaic devices.

I. INTRODUCTION

The transport of excitons - and hence energy - through molecular materials is determined by the exciton transfer integral between neighboring conjugated chromophores. Typically, the length of these chromophores are larger than the distances between them, and thus the usual expression for the transfer integrals, derived by invoking the dipole approximation, is invalid. Indeed, the use of the dipole approximation implies that the exciton transfer integral between equivalent neighboring chromophores scales linearly as the chromophore length. This prediction contradicts the computations of the transfer integrals using various computational techniques, which predict that the transfer integrals vanish in the asymptotic limit[1,2,3,4,5] - a result in agreement with the decreasing Davydov splitting as a function of chromophore length observed in self-assembled molecular aggregates[6].

The exciton transfer integral, J_{mn}, between two polymer chains (or linear conjugated chromophores) m and n is defined by[7],

$$J_{mn} = \sum_{i\in m j\in n} V_{ij} \left[{}_m\langle \mathrm{GS}|\hat{N}_i|\mathrm{EX}\rangle_m \right] \left[{}_n\langle \mathrm{EX}|\hat{N}_j|\mathrm{GS}\rangle_n \right], \tag{1}$$

where $|\mathrm{GS}\rangle_m$ and $|\mathrm{EX}\rangle_m$ are the ground and excited states of polymer m. V_{ij} is the Coulomb interaction between electrons in orbitals ϕ_i and ϕ_j, and $\hat{N}_i$ is the number operator for electrons in orbital ϕ_i. ${}_m\langle \mathrm{GS}|\hat{N}_i|\mathrm{EX}\rangle_m$ is thus the transition density for orbital i on polymer m. When $|\mathbf{r}_i - \mathbf{r}_j|$ is large compared to the interatomic spacing the Coulomb potential is

$$V_{ij} = \frac{\mathrm{e}^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{2}$$

where $\mathbf{r}_i$ is the coordinate of atom i.

In practice, the exact computation of exciton transfer integrals using transition densities is computationally expensive. A convenient approximation is the so-called line-dipole approximation[8,9], which provides a physically intuitive, yet accurate description for exciton transfer when the chromophore separation is large enough (typically, three or four times the monomer length).

In this paper we use the exciton model to explicitly derive the line-dipole approximation. Next, using the line-dipole approximation, analytical expressions for the exciton transfer integral between parallel and collinear conjugated polymers are derived, and the scaling with polymer length is determined. We conclude by discussing the implications of these results for exciton transfer via the Förster mechanism.

Before deriving the line-dipole approximation, however, we review the point-dipole approximation for the evaluation

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of J_{mn}. We define $\tilde{\mathbf{r}}_i$ and $\tilde{\mathbf{r}}_j$ as the site coordinates relative to the center-of-mass of their respective molecules,

$$\begin{aligned}\tilde{\mathbf{r}}_i &= \mathbf{r}_i - \mathbf{R}_m, \\ \tilde{\mathbf{r}}_j &= \mathbf{r}_j - \mathbf{R}_n,\end{aligned} \tag{3}$$

where $\mathbf{R}_m$ and $\mathbf{R}_n$ are the center-of-mass coordinates of molecules m and n, respectively. Then, if

$$|\tilde{\mathbf{r}}_i - \tilde{\mathbf{r}}_j| << |\mathbf{R}_m - \mathbf{R}_n| \equiv |\mathbf{R}_{mn}| \tag{4}$$

we may perform the dipole approximation and write,

$$\sum_{i\in m j\in n} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \approx \frac{\sum_{i\in m} \tilde{\mathbf{r}}_i \cdot \sum_{j\in n} \tilde{\mathbf{r}}_j}{|\mathbf{R}_{mn}|^3} - \frac{3\left(\sum_{i\in m} \mathbf{R}_{mn}\cdot\tilde{\mathbf{r}}_i\right)\left(\sum_{j\in n} \mathbf{R}_{mn}\cdot\tilde{\mathbf{r}}_j\right)}{|\mathbf{R}_{mn}|^5}. \tag{5}$$

Finally, substituting into Eq. (1) gives,

$$J_{mn} = \kappa_{mn} J^0_{mn}, \tag{6}$$

where

$$J^0_{mn} = \frac{[{}_m\langle \mathrm{GS}|\hat{\mu}_m|\mathrm{EX}\rangle_m]\,[{}_n\langle \mathrm{EX}|\hat{\mu}_n|\mathrm{GS}\rangle_n]}{|\mathbf{R}_{mn}|^3}, \tag{7}$$

and

$$\kappa_{mn} = \hat{\mathbf{r}}_m \cdot \hat{\mathbf{r}}_n - 3(\hat{\mathbf{R}}_{mn}\cdot\hat{\mathbf{r}}_m)(\hat{\mathbf{R}}_{mn}\cdot\hat{\mathbf{r}}_n), \tag{8}$$

is an orientational factor. $\hat{\mathbf{r}}_m$ and $\hat{\mathbf{R}}_{mn}$ are the unit vector parallels to $\hat{\mu}_m$ and $\mathbf{R}_{mn}$, respectively. $\hat{\mu}_m$ is the electronic dipole operator for molecule m, defined by

$$\hat{\mu}_m = \mathrm{e}\sum_{i\in m} \tilde{\mathbf{r}}_i \hat{N}_i, \tag{9}$$

and

$${}_m\langle \mathrm{GS}|\hat{\mu}_m|\mathrm{EX}\rangle_m \equiv \mu_N \tag{10}$$

is the transition dipole moment of polymer m with N repeat units.

In practice the condition Eq. (4) is far too severe for conjugated polymers in the solid state, and Eq. (7) is not applicable. However, the much weaker condition that,

$$d << |\mathbf{R}_{mn}|, \tag{11}$$

where d is the monomer size is often satisfied, and under this condition the line-dipole approximation becomes valid.

II. THE LINE DIPOLE APPROXIMATION

In this section the line-dipole approximation will be justified for a simplified model of polymers, namely a chain of dimers (or double bonds) connected by single bonds, as illustrated in Fig. 1. This model is of course applicable to polyacetylene. However, more generally it is also applicable if the dimer represents a monomer.

To derive the line-dipole approximation it is also necessary to introduce a model for excitons in conjugated polymers. In the weak-coupling limit, defined by the electronic band width being greater than the Coulomb interaction, the excited states of conjugated polymers are Mott-Wannier excitons[7,10], defined by

$$|EX\rangle = \sum_{r,R} \psi(r)\Psi(R)|R,r\rangle, \tag{12}$$

where $|R,r\rangle$ is an electron-hole basis state,

$$|R,r\rangle = \frac{1}{\sqrt{2}}\left(c^{c\dagger}_{R+r/2,\uparrow} c^{v}_{R-r/2,\uparrow} + c^{c\dagger}_{R+r/2,\downarrow} c^{v}_{R-r/2,\downarrow}\right)|\mathrm{GS}\rangle. \tag{13}$$

$c^{c\dagger}_{R+r/2,\sigma}$ creates an electron with spin σ in the conduction band Wannier orbital at $R + r/2$, while $c^{v}_{R-r/2,\sigma}$ destroys an electron with spin σ in the valence band Wannier orbital at $R - r/2$, and $|\mathrm{GS}\rangle$ is the ground state. $\psi(r)$ is the 'hydrogenic' wavefunction for the particle-hole pair, where r is the relative coordinate. $\Psi(R)$ is the center-of-mass envelope wavefunction, where R is the center-of-mass coordinate.

To a good approximation it can be shown[7] that the transition densities satisfy,

$$\langle \mathrm{GS}|\hat{N}_i|\mathrm{EX}\rangle = \Psi(R_{\ell_i}) \left(\frac{\psi(0)}{\sqrt{2}}\right) (-1)^{i+1}. \tag{14}$$

We note that the transition densities are modulated by the center-of-mass wavefunction and alternate in sign, as illustrated for the lowest excited exciton in Fig. 1.

Using Eq. (14), Eq. (1) now becomes,

$$J_{mn} = \left(\frac{\psi(0)^2}{2}\right) \sum_{i\in m} \sum_{j\in n} V_{ij} \Psi(R_{\ell_i}) \Psi(R_{\ell_j}) (-1)^{i+1} (-1)^{j+1}, \tag{15}$$

To simplify this expression it is convenient to partition the sum over sites, i, as a sum over unit cells, ℓ, and a sum over sites within a unit cell:

$$J_{mn} = \left(\frac{\psi(0)^2}{2}\right) \sum_{\ell_i\in m} \sum_{\ell_j\in n} \Psi(R_{\ell_i}) \Psi(R_{\ell_j}) \left\{ \sum_{i=1,2} \sum_{j=1,2} V_{ij} (-1)^{i+1} (-1)^{j+1} \right\}. \tag{16}$$

Then, if the unit cell size, d, satisfies,

$$d << r_{\ell_i \ell_j}, \tag{17}$$

where $r_{\ell_i\ell_j}$ is the distance between the unit cells, the term in curly parentheses can now be simplified using the dipole approximation to become,

$$\sum_{i=1,2} \sum_{j=1,2} V_{ij} (-1)^{i+1} (-1)^{j+1} = \frac{\mathrm{e}^2 a^2 \kappa_{\ell_i \ell_j}}{r^3_{\ell_i \ell_j}}, \tag{18}$$

and thus,

$$J_{mn} = \mu_1^2 \sum_{\ell_i\in m} \sum_{\ell_j\in n} \Psi(R_{\ell_i}) \frac{\kappa_{\ell_i\ell_j}}{r^3_{\ell_i\ell_j}} \Psi(R_{\ell_j}). \tag{19}$$

μ_1 is the transition dipole moment of a dimer, defined by

$$\mu_1 = \frac{\mathrm{e} a \psi(0)}{\sqrt{2}} \tag{20}$$

and a is the bond length. Since μ_1 is independent of the length of the polymer, Eq. (19) reveals how the exciton transfer integral varies with the polymer length, as will be described in the next section. However, an alternative representation of Eq. (19) will now be derived which makes a more direct comparison to the point-dipole approximation and introduces the line-dipole approximation.

Using the expression for the transition dipole moment of the whole chain (from Eq. (9), Eq. (10), and Eq. (14))[7], namely

$$\mu_N = \mu_1 \sum_{\ell} \Psi(R_\ell), \tag{21}$$

where the sum is over unit cells, Eq. (19) can be re-expressed as:

$$J_{mn} = \left(\frac{\mu_N}{\sum_\ell \Psi(R_\ell)}\right)^2 \sum_{\ell_i\in m} \sum_{\ell_j\in n} \Psi(R_{\ell_i}) \frac{\kappa_{\ell_i\ell_j}}{r^3_{\ell_i\ell_j}} \Psi(R_{\ell_j}). \tag{22}$$

This expression for the transfer integral between conjugated polymers justifies the line-dipole approximation as may be seen as follows. Using Eq. (21), the transition dipole moment for a polymer of N monomer units may be written as a sum of the transition dipole moments for each monomer, namely

$$\mu_N = \sum_\ell \mu(R_\ell), \tag{23}$$

where

$$\mu(R_\ell) \equiv \mu_1 \Psi(R_\ell) = \mu_N \frac{\Psi(R_\ell)}{\sum_\ell \Psi(R_\ell)}. \tag{24}$$

Assuming that each monomer of polymer m interacts with each monomer of polymer n via the point-dipole approximation, the total exciton integral between the polymers is[9],

$$J_{mn} = \sum_{\ell_i \in m} \sum_{\ell_j \in n} \mu(R_{\ell_i}) \frac{\kappa_{\ell_i \ell_j}}{r^3_{\ell_i \ell_j}} \mu(R_{\ell_j}). \tag{25}$$

Eq. (22) is thus derived by inserting Eq. (24) into Eq. (25).

Before discussing the evaluation of Eq. (19) and its validity, we describe the standing-wave and plane-wave approximations for the center-of-mass wavefunction, $\Psi(R_\ell)$.

A. Standing waves

For linear polymers with N equivalent monomers and open boundary conditions the exciton center-of-mass wavefunction satisfies,

$$\Psi(R_\ell) = \sqrt{\frac{2}{N+1}} \sin(\beta R_\ell), \tag{26}$$

where β is the pseudo-momentum of the center-of-mass, defined by $\beta = \pi j /(N+1)$ with $1 \le j \le N$. This form of $\Psi(R_\ell)$ in Eq. (21) gives

$$\begin{aligned} \mu_N = &\quad \mu_1 \sqrt{\frac{2}{N+1}} \cot(\beta/2) \\ \sim &\quad \sqrt{N}/j, \end{aligned} \tag{27}$$

when $N/j \gg 1$. We therefore see that in the point-dipole approximation $J \sim L$.

B. Plane waves

In the next section it will be expedient to employ the plane wave approximation for $\Psi(R_\ell)$ valid for translationally invariant systems,

$$\Psi(R_\ell) = \frac{\exp(iKR_\ell)}{\sqrt{N}}, \tag{28}$$

where K is the Bloch momentum of the center-of-mass, defined by $K = 2\pi j/Nd$ with $-N/2 \le j \le N/2$. This approximation allows analytical expressions to be derived for the exciton transfer integral, although it is less applicable than the standing wave approximation in linear conjugated polymers and chromophores.

C. Validity of the Line-dipole approximation

The validity of the line-dipole approximation has already been discussed elsewhere (see ref.[8] and references therein). When $R = d$ there is a significant error in the line-dipole approximation result. However, for $R \gtrsim 2d$ the line-dipole approximation result is in good agreement with the exact result for short chains, becoming essentially exact for all chain lengths when $R \gtrsim 3d$.

D. Parallel Chains

An analytical expression can be derived for the transfer integral in the continuum limit assuming the plane wave form for the center-of-mass wavefunctions, Eq. (28). Then,

$$J \approx \frac{\mu_1^2}{Ld} \int_0^L \int_0^L \frac{(1 - 3\cos^2\theta)}{r^3} dx_1 dx_2, \tag{29}$$

where r is the distance between the segments at x_1 on chain 1 and x_2 on chain 2. For parallel chains with $D = D_0 = 0$ the computation of Eq. (29) gives,

$$J = \left(\frac{2\mu_1^2}{RLd}\right)\left(1 - \frac{R}{(R^2 + L^2)^{1/2}}\right). \tag{30}$$

The dependence of the exciton transfer integral on the polymer length is made more explicit by defining J as,

$$J = \left(\frac{2\mu_1^2}{R^2 d}\right) g(\tilde{L}), \tag{31}$$

where $g(\tilde{L})$, the dimensionless exciton transfer integral, is

$$g(\tilde{L}) = \frac{1}{\tilde{L}}\left(1 - \frac{1}{\sqrt{(1 + \tilde{L}^2)}}\right) \tag{32}$$

and $\tilde{L} = L/R$.

$g(\tilde{L})$ is plotted versus $\tilde{L}$ for $R = 5d$ in Fig. 2 and Fig. 3. As $\tilde{L} \to 0$ (or $L << R$) $g(\tilde{L}) \to \tilde{L}/2$ and thus $J \sim LR^{-3}$, confirming the point-dipole approximation for the whole chain. Conversely, as $\tilde{L} \to \infty$ (or $L >> R$) $g(\tilde{L}) \to \tilde{L}^{-1}$ and thus $J \sim (RL)^{-1}$. The maximum value of g is $g_{\max} \approx 0.300$, occurring at

$$\tilde{L}_{\max} = \left(\frac{1 + \sqrt{5}}{2}\right)^{1/2} \approx 1.2720\cdots \tag{33}$$

These idealized analytical results are consistent with the quantum chemistry calculations on explicit polymer systems of other authors[2,3,4,5].

It is also instructive to express J as,

$$J = \left(\frac{\mu_N^2}{R^3}\right) f(\tilde{L}), \tag{34}$$

where

$$f(\tilde{L}) = \frac{2}{\tilde{L}^2}\left(1 - \frac{1}{\sqrt{(1 + \tilde{L}^2)}}\right) \tag{35}$$

can be regarded as a correction to the point-dipole approximation for the whole chain. As $\tilde{L} \to 0$ $f(\tilde{L}) \to 1$, while as $\tilde{L} \to \infty$ $f(\tilde{L}) \to 2\tilde{L}^{-2}$. $f(\tilde{L})$ is plotted in Fig. 4.

The analytical results derived in this section have assumed the plane-wave approximation for the exciton center-of-mass wavefunction. A more realistic approximation for linear polymer chains, however, is the standing-wave approximation, Eq. (26). Analytical expressions cannot be derived using this form of Ψ. However, Eq. (19) is easily evaluated numerically. Fig. 2 and Fig. 3 show $g(\tilde{L})$ in this approximation. For $\tilde{L} \lesssim 20$ the plane and standing wave approximations agree rather well. However, the asymptotic behavior is different, decreasing more rapidly with chain length for the standing wave approximation, namely $g(\tilde{L}) \sim \tilde{L}^{-1.8}$, as indicated in Fig. 3.

E. Collinear Chains

For collinear chains with $R = 0$, $D_0 = L$, and D arbitrary, the evaluation of Eq. (29) for the plane-wave approximation gives,

$$J = -\left(\frac{2\mu_1^2}{D^2 d}\right)\frac{L}{(L+D)(2L+D)}, \tag{36}$$

or

$$J = -\left(\frac{2\mu_1^2}{D^2 d}\right) g(\tilde{L}) \tag{37}$$

where

$$g(\tilde{L}) = \frac{\tilde{L}}{(\tilde{L}+1)(2\tilde{L}+1)} \tag{38}$$

and $\tilde{L} = L/D$. $g(\tilde{L})$ is plotted versus L/D for $D = 5d$ in Fig. 5 and Fig. 6. As $\tilde{L} \to 0$ $g(\tilde{L}) \to \tilde{L}$, while as $\tilde{L} \to \infty$ $g(\tilde{L}) \to (2\tilde{L})^{-1}$. The maximum value of g is $g_{\max} \approx 0.172$, occurring at $\tilde{L}_{\max} = 1/\sqrt{2}$.

Fig. 5 and Fig. 6 also show the numerical evaluation of the transfer integral using the standing-wave approximation for the exciton center-of-mass wavefunction. In this case, as $\tilde{L} \to \infty$ $g(\tilde{L}) \sim \tilde{L}^{-2}$.

For collinear chains J can also be expressed as a correction to the point-dipole approximation for the whole chain as,

$$J = -\left(\frac{2\mu_N^2}{D^3}\right) f(\tilde{L}), \tag{39}$$

where

$$f(\tilde{L}) = \frac{1}{(\tilde{L}+1)(2\tilde{L}+1)}. \tag{40}$$

This function is plotted in Fig. 4.

III. DISCUSSION AND CONCLUDING REMARKS

In this paper the line-dipole approximation for the evaluation of the exciton transfer integral, J, between conjugated polymer chains has been rigorously justified for a chain of dimers. Quite generally, it is physically reasonable to apply this approximation to a conjugated polymer or linear chromophore with general monomeric units.

Then, using the line-dipole approximation, as well as the plane-wave approximation for the exciton center-of-mass wavefunction, it has been shown analytically that $J \sim L$ when the chain lengths are smaller than the separation between them, where L is the polymer length. However, when the chain lengths are larger than their separation, J is a decreasing function of chain length, scaling as L^{-1} for the plane-wave approximation. Scaling relations have also been obtained numerically for the more realistic standing-wave approximation for the exciton center-of-mass wavefunction, where it is found that for chain lengths larger than their separation $J \sim L^{-1.8}$ or $J \sim L^{-2}$, for parallel or collinear chains, respectively.

The scaling of $J \sim L$ for short chain lengths is a reflection of the fact that at these lengths scales the point-dipole approximation may be applied to the entire chain, implying that $J \propto \langle \mathrm{GS}|\hat{\mu}|\mathrm{EX}\rangle^2 \sim L$. Similarly, the scaling of $J \sim L^{-1}$ for collinear chains in the plane-wave approximation is easy to understand for chain lengths large compared to their separation. In this case the exciton dipoles are uniformally distributed along both chains of length L. The double line integral of r^{-3} trivially gives the L^{-1} scaling.

The scaling of J with L for long *parallel* chains is rather counter-intuitive, however, as it implies (as discussed below) that the probability of exciton transfer between neighboring parallel chains is a decreasing function of length. The physical origin of this behavior can be understood in two ways. First, consider the exciton transfer integral for parallel chains when their separation is of the order of the monomer length (d). In this limit J is a periodic function of the relative shift variable D[1]. Fig. 7 shows J for $D = 0$ (the in-phase configuration), $D = a$ (the out of phase configuration), and $D = a/2$ (the phase-cancelation configuration), illustrating this periodic variation. As the separation between parallel chains increases this periodic variation vanishes because of interference effects from longer

distance transition densities. It is these interference effects that mean ultimately the exciton transfer integral must vanish in the asymptotic limit for chain separations greater than a few monomer lengths.

A second way to motivate this scaling behavior is to consider the sign of J as two finite-length dipoles are moved longitudinally relative to another. As they slide passed each other the sign of J will change once the magic angle ($\theta = \cos^{-1}(1/\sqrt{3})$) is reached. Evidently, in the limit of infinitely long chains this thought-experiment is nonsensical, implying that $J = 0$.

The results for the exciton transfer integral have been derived using the assumption that the exciton center-of-mass wavefunction, Ψ, is described either by a standing wave or a plane wave. The standing wave approximation is more relevant than the plane wave approximation in linear conjugated polymers or chromophores, although the plane wave approximation enables analytical results to be derived. In reality, however, disorder or self-trapping will modify the exciton center-of-mass wavefunction from both of these idealized functional forms, and under these circumstances it is necessary to evaluate Eq. (19) with the explicit form of Ψ. Such a calculation is beyond the scope of the present paper.

The results presented in this paper have important implications for the photo-physics of conjugated polymers and self-assembled molecular systems. First, as already reported[1,2,3,4,5], the Davydov splitting in aggregates is a decreasing function of chain length for chain lengths larger than their separation. Second, the Förster transfer rate, k, is reduced by a factor of $f^2(\tilde{L})$, where $f(\tilde{L})$ is the correction to the point-dipole approximation for the entire chain, shown in Fig. 4. This conclusion may be understood by noting that in the point-dipole approximation,

$$k \propto \frac{1}{R^6} \int_0^\infty \frac{I_D(\omega)\alpha_A(\omega)}{\omega^4} d\omega, \tag{41}$$

where $I_D(\omega)$, the donor emission spectrum, and $\alpha_A(\omega)$, the acceptor absorption spectrum, are both proportional to the square of the transition dipole moments. In the line-dipole approximation, therefore, there is a correction of $f(\tilde{L})$ for each of these squared transition dipole moments. This latter result has obvious important deleterious consequences for the performance of polymer photovoltaic devices where exciton migration occurs via Förster transfer between neighboring conjugated polymers or chromophores.

Acknowledgments

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Figure Captions

FIG 1: The geometry of two conjugated polymers. R is the transverse separation and $D_0 + D$ is the longitudinal shift. Also shown are the sign of the transition densities for the lowest excited exciton, the site labels '1' and '2' in a unit cell, and the definitions of a, d, L, and θ. For parallel chains $D_0 = 0$, while for collinear chains $R = 0$ and $D_0 = L$.

FIG 2: The dimensionless exciton transfer integral, $g(R, L) = JR^2 d/2\mu_1^2$, evaluated for parallel chains ($D_0 = D = 0$) using the line-dipole approximation with the plane-wave approximation Eq. (28) (solid curve) and the standing wave approximation Eq. (26) (dashed curve) for the exciton center-of-mass wavefunction. The inter-chain separation $R = 5d$, where d is the monomer length.

FIG 3: As for Fig. 2

FIG 4: The correction function, $f(\tilde{L})$, for the point-dipole approximation. Solid curve: parallel chains where $\tilde{L} = L/R$; dashed curve: collinear chains where $\tilde{L} = L/D$.

FIG 5: The dimensionless exciton transfer integral, $g(D, L) = JD^2 d/2\mu_1^2$, evaluated for collinear chains ($R = 0$ and $D_0 = L$) using the line-dipole approximation with the plane-wave approximation Eq. (28) (solid curve) and the standing wave approximation Eq. (26) (dashed curve) for the exciton center-of-mass wavefunction. The chain separation $D = 5d$, where d is the monomer length.

FIG 6: As for Fig. 5.

FIG 7: The dimensionless exciton transfer integral, $g(R, L) = JR^2 d/2\mu_1^2$, evaluated for parallel chains ($D_0 = 0$) using transition densities (solid lines) and the line-dipole approximation (dashed lines). The inter-chain separation, $R = d$. The longitudinal shift, D, is $D = 0$ (circles), $D = a/2$ (no symbols), and $D = a$ (diamonds).

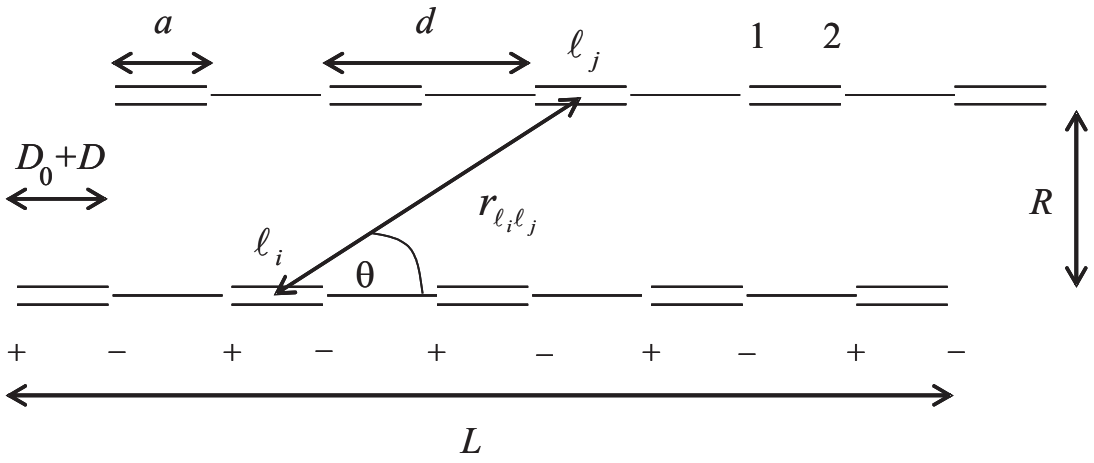
a
d
ℓ_j
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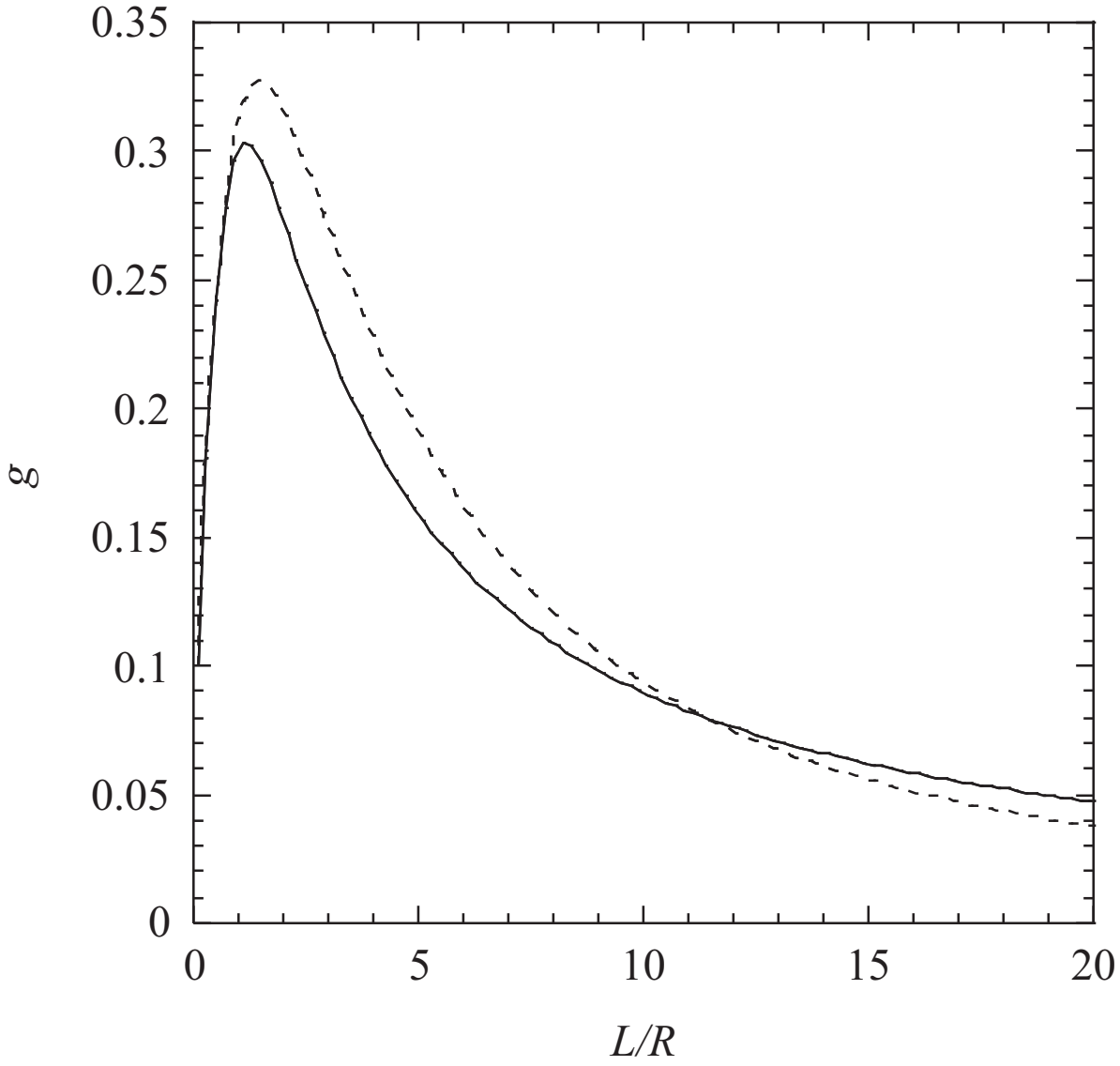
FIG. 1:


0.35
0.3
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0.15
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g
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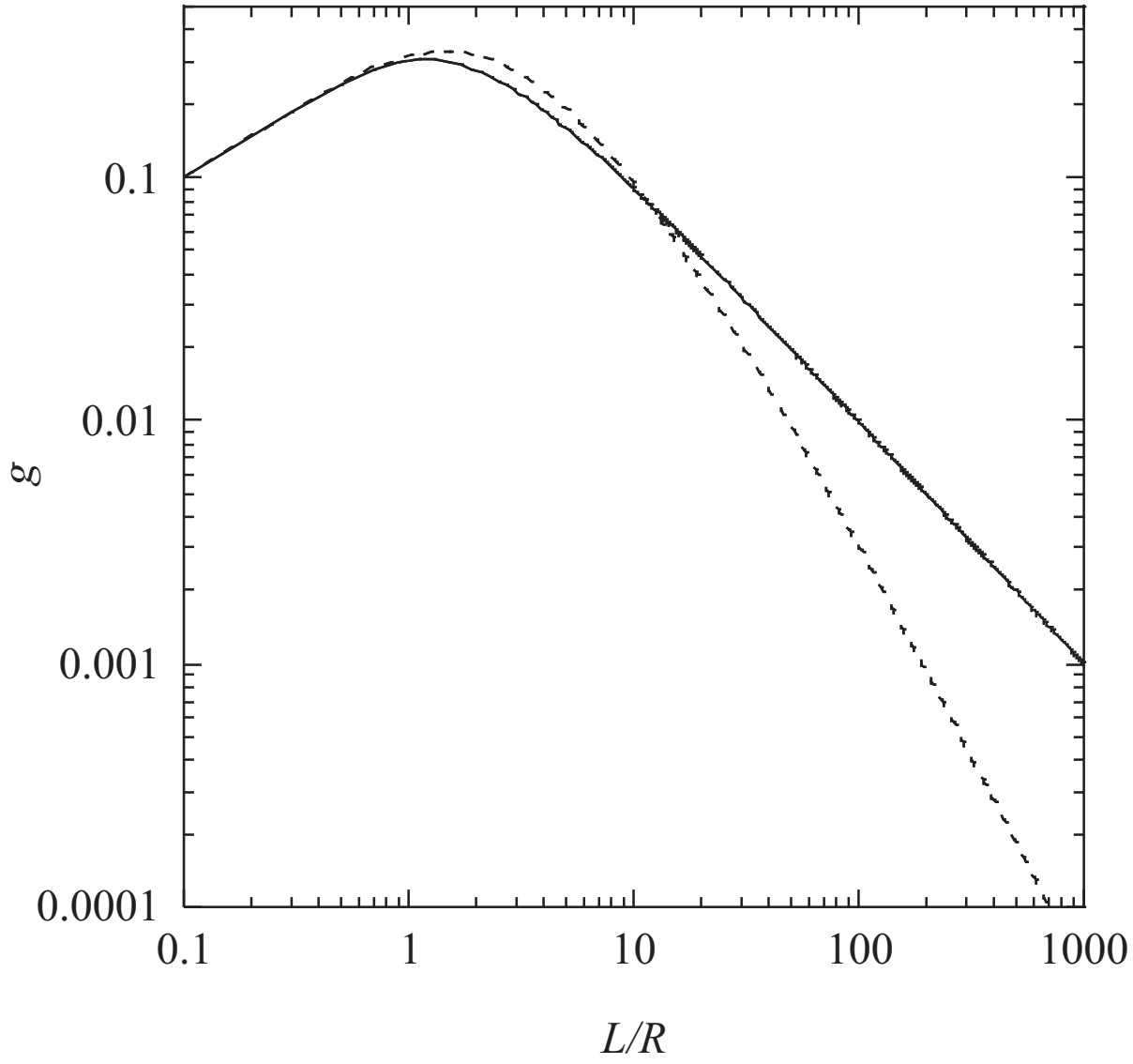
5
10
15
20
L/R

FIG. 2:


0.1
0.01
0.001
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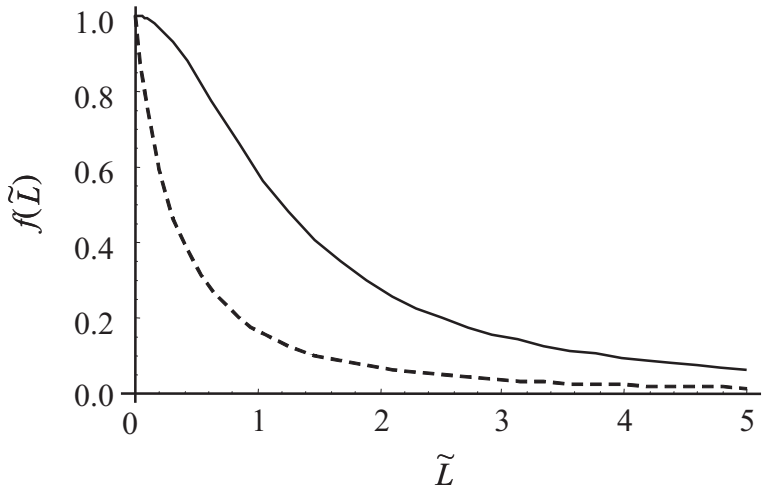
g
0.1
1
10
100
1000
L/R

FIG. 3:


1.0
0.8
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0.0
f(L̃)
0
1
2
3
4
5
L̃

FIG. 4:

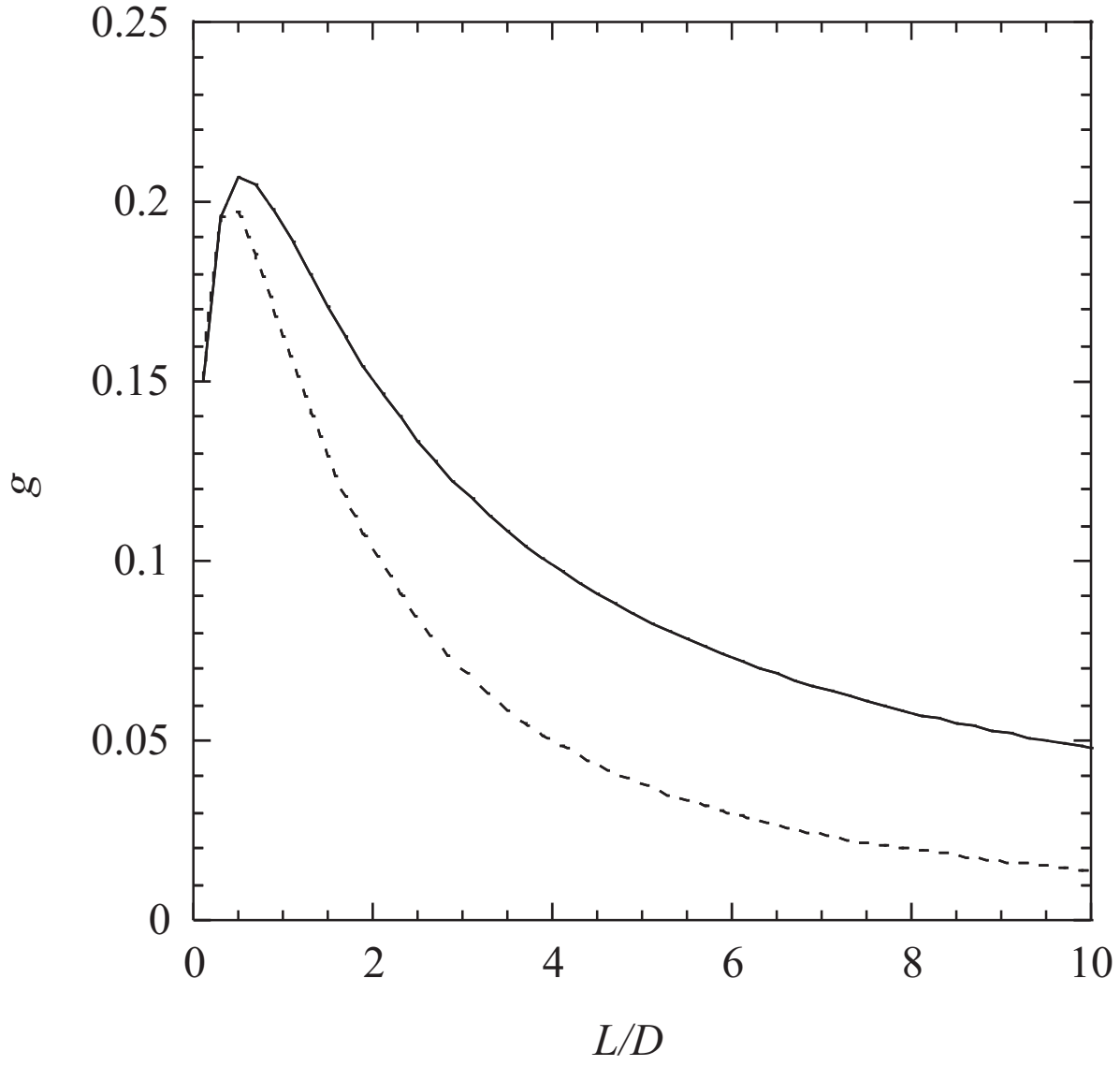

FIG. 5:

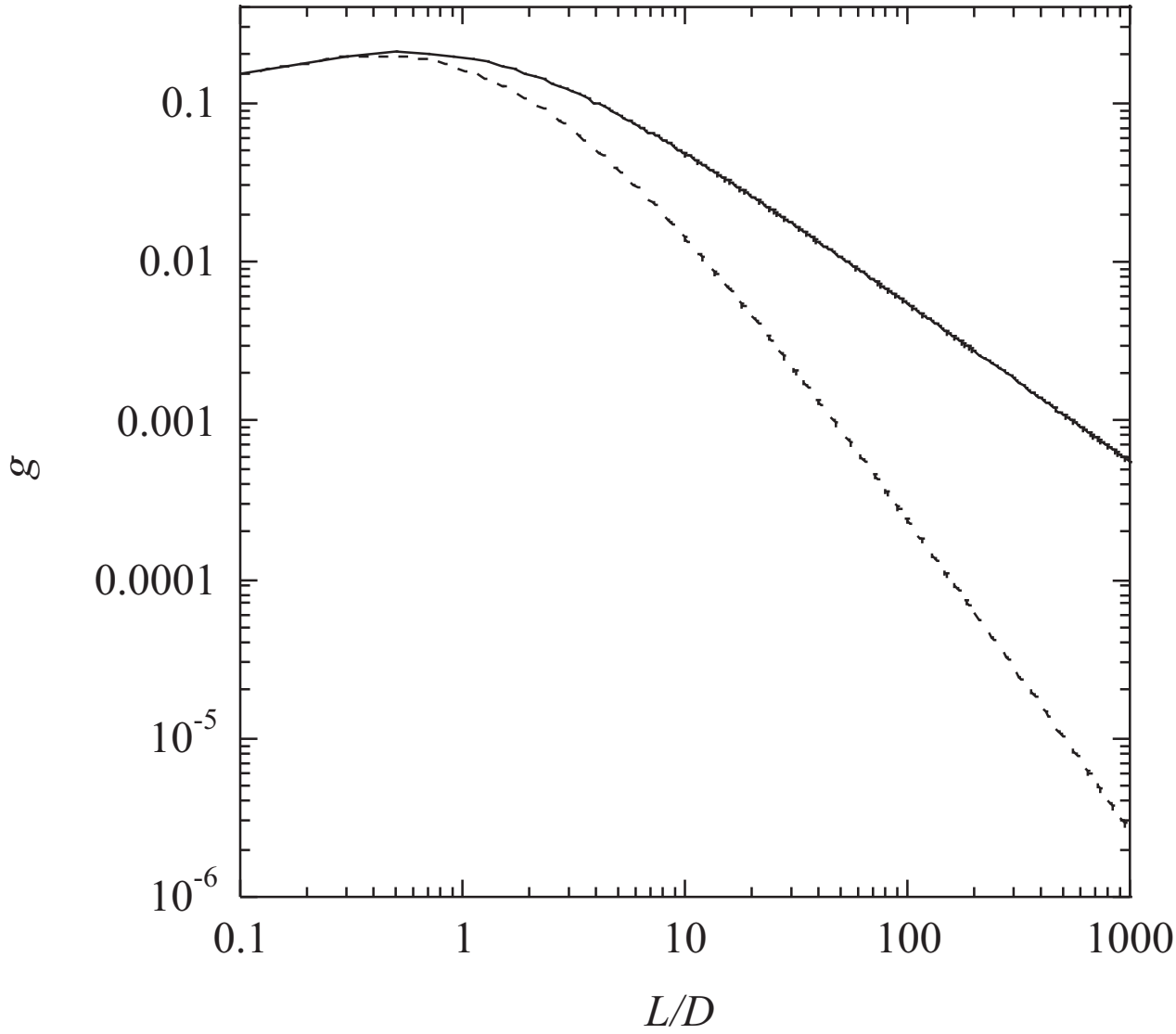

FIG. 6:

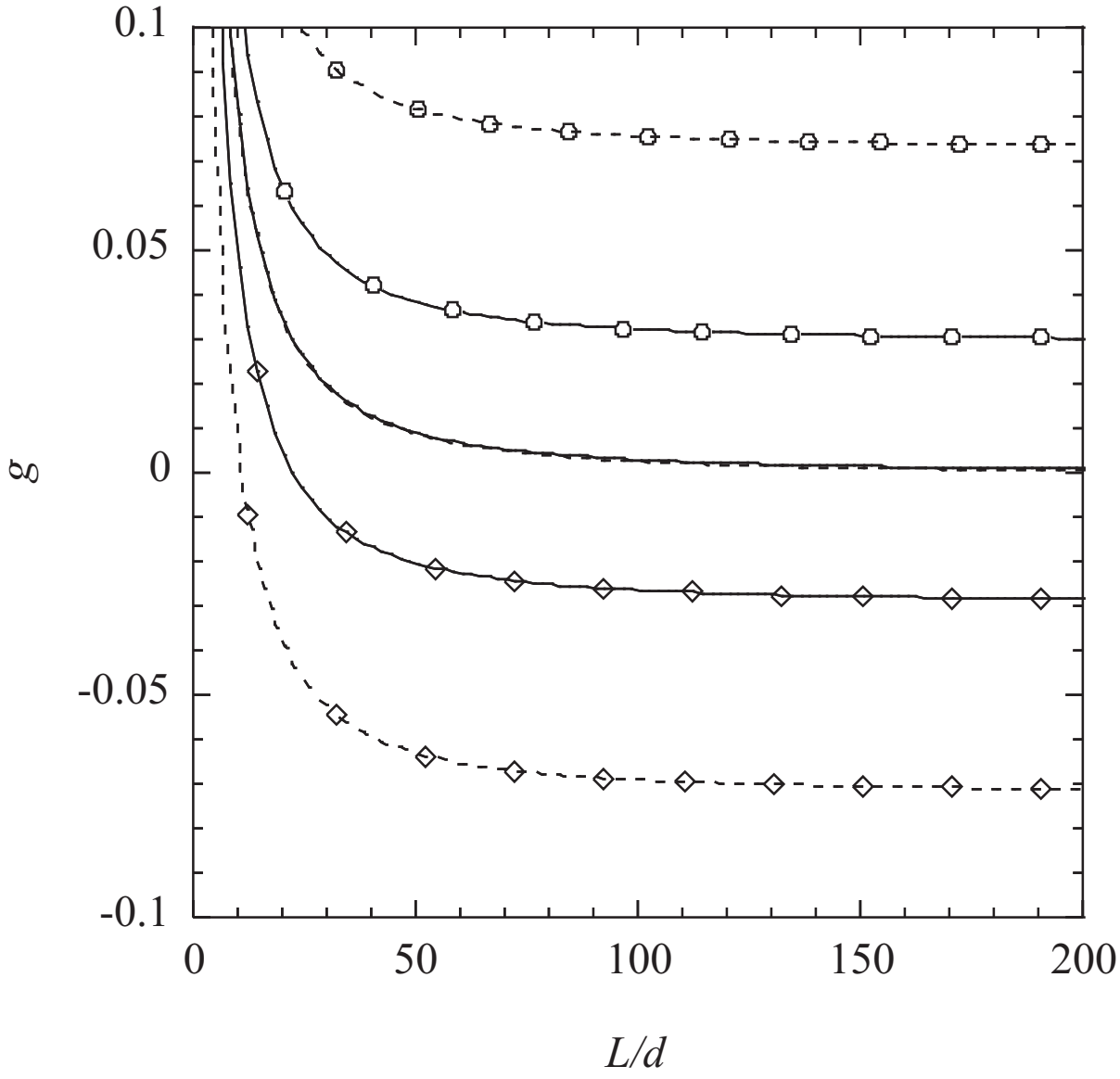

FIG. 7: